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(54) **Process for upgrading metal powder**

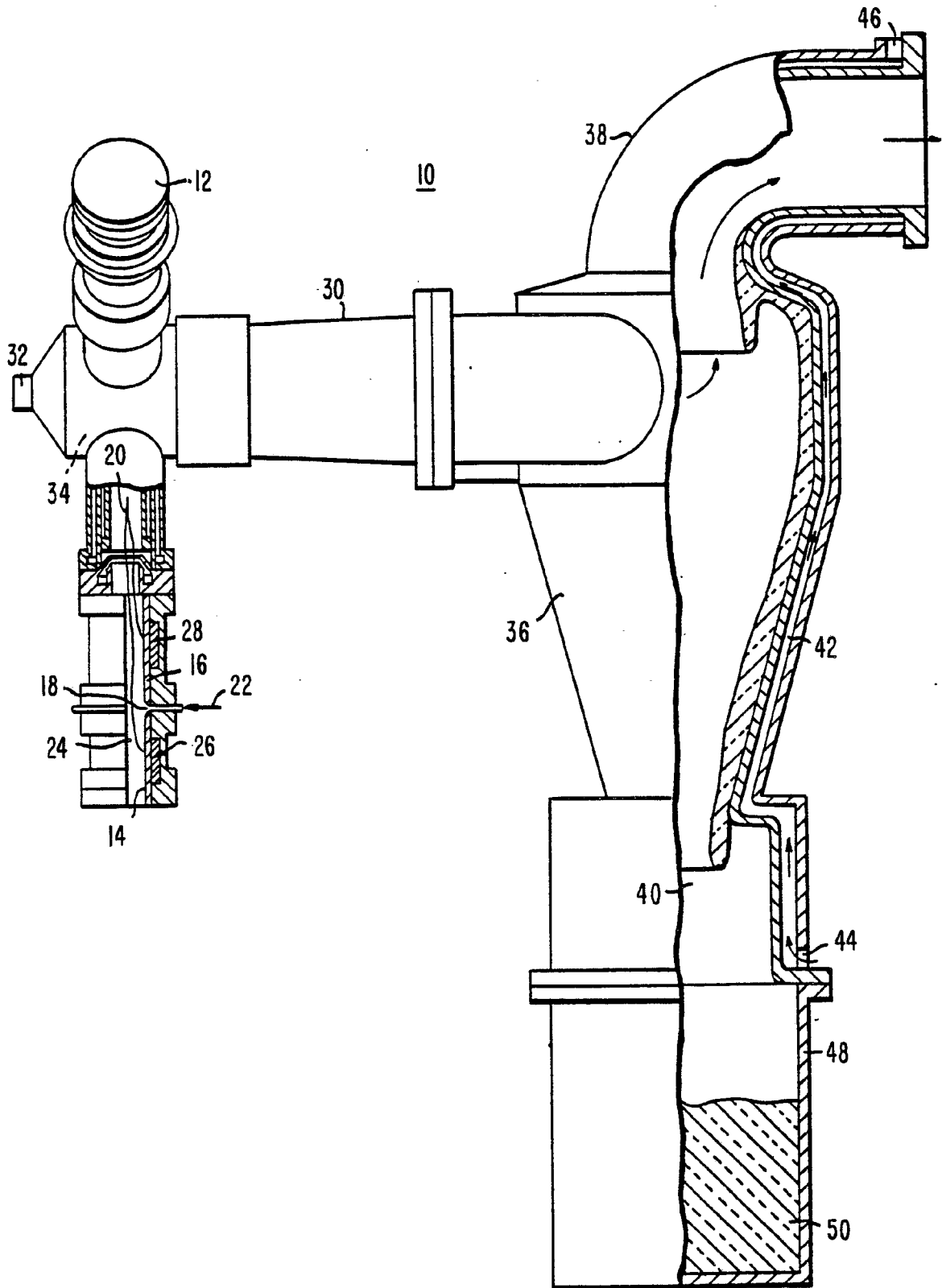
(57) A method for upgrading commercially available titanium, zirconium or hafnium powder containing chloride contaminant is characterized by the step of contacting the metal powder with an inert gaseous plasma (such as the arc heated stream of an arc heater) for a sufficient time to effect physical separation of metal and contaminant salt. By operating the arc heater at

temperatures in excess of the boiling point of the contaminant salt (e.g. above 1686°K for NaCl) the purification can be assisted by vaporization of the salt. After quenching and cooling the upgraded metal powder, any residual contaminant salt on the surface of the metal can be removed by water washing. The upgraded metal powder produced is useful in fabricating high density metal alloy parts by the blended elemental powder metallurgical process.

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SPECIFICATION

Process for upgrading metal powder

This invention relates to a process for upgrading titanium, zirconium or hafnium powder.

5 More specifically, it relates to a method of plasma purification of titanium, zirconium or hafnium powder.

The properties of high corrosion resistance and strength combined with a relatively low density, result in titanium alloys being ideally suited to many applications such as the aerospace industry. Zirconium with the additional property of relatively low neutron cross-section and hafnium with high neutron cross-section result in these metals being ideally suited to many applications in the nuclear energy field. However, the widespread use of such metals has been and continues to be severely limited by their high cost which is a direct consequence of the high energy consumption and the batch nature of conventional metal production and of the amount of waste in producing finished parts. For example, for every pound of titanium fabricated in the form of a part, as much as seven or eight pounds of titanium can be wasted. Similarly considerable scrap is generated in processing and fabricating zirconium and hafnium, thus generally necessitating a cost saving, yet expensive, step of reprocessing the scrap.

30 One of the most promising techniques to circumvent the high cost of fabricated metal parts is powder metallurgy (PM). This technology essentially involves the known steps of powder production followed by compaction into a solid article. Historically, two different processes have been developed for PM production of fabricated metal parts. One involves hot isostatic pressing of pre-alloyed powders and the other involves cold compaction and subsequent sintering of blended elemental powders. However, considerable development is still required to optimize either process such that the final product possesses at least equal properties and lower cost than the corresponding forged wrought metal part.

45 Since titanium powder is quite soft and ductile and because such titanium powders are already commercially available, the PM route to titanium alloy parts involving the direct blending of the elemental metal powders before compaction, in principle, is very economically attractive. Presently, however, titanium sponge from the known commercial Kroll and/or Hunter processes that has been ground into a powder exhibits a major drawback in that the high residual impurity content, principally from chlorides (e.g. typically 0.15 weight per cent for titanium and 0.5 weight per cent for zirconium), results in high porosity in the final PM fabricated material. For example, in a recent article by P. R. Anderson and P. C. Eloff published as part of The Metallurgical Society of AIME's 109th annual meeting, February 26—28, 1980, pages 175 through 187, a high density PM (titanium, vanadium, aluminum) material was fabricated into a finished part by the blended

65 elemental processing technique and properties in excess of the minimum specified properties of forged wrought titanium/aluminum/vanadium were achieved. However, the residual chlorine content was observed to have a strong deleterious effect on the microstructure of the high density titanium alloy product (see conclusions, page 180). Thus, the need for an economical method of reducing the sodium chloride content of commercially available titanium powder still exists.

70 It is also generally known that certain high melting point, refractory powders can be spheroidized by plasma processing (see for example an article by M. G. Fey, C. B. Wolf and F. J. Harvey, entitled "Magnetite Spheroidization Using an Alternating Current Arc Heater", I and EC Process Design and Development, Vol. 16, pages 108+, January, 1977, and a preceding publication by F. J. Harvey, T. N. Meyer, R. E. Kothmann and M. G. Fey entitled "A Model of Particle Heat Transfer in Arc Heated Gas Streams" (published in "Proceedings of International Roundtable on Study and Applications of Transport Phenomena in Thermal Plasmas", IUPAC-CMRS, Odeillo, France, 1975).

80 Accordingly, the present invention resides in a process for upgrading metal powder which comprises establishing a plasma within a plasma reactor; feeding powdered titanium, zirconium or hafnium containing at least one alkali metal or alkaline earth metal halide salt contaminant, through said plasma thus effecting a physical separation of said metal and contaminant salt; cooling said metal; and recovering an upgraded metal.

95 The intention is to upgrade a finely divided commercial metal powder containing, as contaminant, an alkali metal or alkaline earth metal halide salt. After passing through the plasma stream, the metal can be quenched downstream from the plasma and thus be recovered as an upgraded powder. Advantageously, the physical separation (i.e., the plasma heating) is performed at a temperature above the boiling point of the contaminant salt (e.g. NaCl, MgCl₂) thus vaporizing the contaminant salt. Consequently it should be possible to collect the metal and salt separately. Subsequent washing can be used, if necessary, to remove residual contaminant from the surface of the purified metal.

110 By economically upgrading commercially available titanium powder or sponge (or the equivalent such as Zr and Hf) produced by the Kroll or Hunter processes, it becomes amenable to fabrication of high density parts by the blended elemental powdered metallurgy process, the powder has a reduced chloride content and the particle size of the final product is controlled including the ability, if desirable, to produce a spheroidized purified powder.

125 Preferably, a plasma reactor is used which incorporates a plasma producing source. This plasma source can be an arc heater (plasma

torch) or the plasma can be generated without the use of an electric arc; e.g. by a radio frequency torch.

In order that the invention can be more clearly understood, a convenient embodiment thereof will now be described, by way of example, with reference to the accompanying drawing which is a cut-away view of a plasma reactor for use in upgrading metal powder.

Referring to the drawing, plasma reactor system 10 comprises one or more, preferably three, arc heaters 12, (two of which are shown) which are similar in operation and construction to those described in U.S. Patent Specification Nos. 3,705,975 and 3,832,519. In view of the full disclosure in those patent specifications, the description of the arc heaters 12 is limited herein to the basic structure and operation. Each arc heater 12 is a single-phase self-stabilizing AC device capable of power levels up to about 3500 kilowatts, or up to about 10,000 kilowatts for the three-phase plant installation. In the practice of this invention, it is preferred that three arc heaters 12 are provided, one for each of the three phases of the AC power supply.

Each arc heater 12 has two annular copper electrodes 14 and 16 which are spaced at gap 18 about one millimeter apart to accommodate a line frequency power source of about 4 kV. An arc 20 occurs in the space or gap 18 and incoming inert gas at inlet 22 blows the arc 20 from the space into the interior of an arc chamber 24. The gas entering at inlet 22 must be compatible with the metal being upgraded and may be one of the gases selected from the group consisting of an inert gas, hydrogen, or a mixture thereof. The inert gas is preferably argon. The arc 20 rotates at a speed of about 1000 RPS by interaction of the arc current (up to several thousand amps AC) and a DC magnetic field set up by internally mounted field coils 26 and 28.

The velocities yield a very high operating efficiency for equipment of this type and the elongated arc 20 is ultimately projected by the gas downstream into a plenum chamber 30. Feedstock metal powders including titanium, zirconium or hafnium are introduced under pressure, through inlet 32 where they are heated by direct contact with the plasma heated gases.

As shown in the drawing the arc heaters 12 are mounted on a tubular member 34 and extending radially therefrom. The member 34 is preferably cylindrical and forms the plenum chamber 30. The member 34 is connected to the separator 36 tangentially to enhance centrifugal separation of the gaseous and particulate products of the upgrading reaction, whereby the lighter gaseous products, such as the contaminant salts, leave the separator through an outlet means 38, while the heavier powdered titanium, zirconium or hafnium exit through an outlet 40 at the lower end of the separator. The separator is cooled by cooling jacket means 42 having a cooling water inlet 44 and an outlet 46. The resulting metal product

drops into the crucible 48 wherein an upgraded powder 50 is collected.

During operation of the arc heater, an electrical arc is first established between the copper electrodes 14 and 16. The pressurized stream or sheath of inert gas (such as argon, helium or the like) is introduced through the inlet 22 located between the electrodes. In this manner, the length of the plasma arc 20 is extended towards the plenum chamber 30 and the pathway of the metal powder to achieve the desired thermal contact and residence time. Preferably, a minimum flow rate of inert gas is to be used at a given particle feed rate. Particle flow rate and plasma power (temperature) should be regulated such that the metal melts but does not significantly vaporize as this would lead to ultrafine material. The residence time and heat transfer achieved in the arc plasma can be calculated according to known principles. The mathematical modeling of the heat transfer involved in the arc heater is more fully described in the previously mentioned F. J. Harvey et al. IUPAC reference and is incorporated herein by reference for such purposes. Similarly, the overall process and associated apparatus for operation of an arc heater is described more fully in U.S. Patent Specification Nos. 4,080,194 and 4,107,445.

The quenching or cooling chamber can essentially be any such device known in the art. Preferably, the cooling tower walls are double walled or tube traced with internal coolant circulation being employed for heat transfer control. The overall chamber can also be internally sleeved with selected ceramic cylindrical liners to vary the quenching conditions or to collect the product by condensation on the wall, again as known in the art. A variety of product collection means can be incorporated into the plasma reactor. Thus as illustrated a cyclone separator 36 can be used or a system of filters, electrostatic precipitation or the like can be employed.

It is envisioned that as the contaminated metal powder particles enter and pass through the plasma heated gases, the lower melting and more volatile contaminant liquefies and tends to escape the interstices of the sponge fines as vapors. With sufficient residence time in the plasma stream, the metal melts and the overall process can be viewed as a melting down and phase separation on an individual particle basis. As the solid particles melt, they contract under the influence of surface tension forces in a molten droplet. The spherical shape is retained after the particle has cooled to a solid. The manner in which the droplets are quenched and collected will determine the exact nature of the product and several possibilities exist. If the individual metal particles are collected while the contaminant salt is still gaseous (i.e., at high temperature) with the use of a cyclone or the like, an efficient separation and high purity product is achieved in one step. However, such a scheme involves the use of expensive high temperature collecting

equipment and the possibility that the resulting hot powder will self-bond. Alternately, the upgraded metal powder exiting the plasma stream can be rapidly quenched and collected at a lower temperature without risk of particle agglomeration. These alternatives are viewed as being capable of producing either an upgraded spherical powder at temperatures above the melting point of the metal or upgraded rough sponge particles at lower temperatures without significantly altering the particle size distribution. However, in this case, the possibility of discreet contaminant particles comingling or adhering to the metal particles or the partial coating of the metal particles with a layer of solid contaminant is increased. If insufficient separation occurs, a subsequent washing step with water or mild acid solution or the like can be employed. The aqueous acid wash step can also be advantageously employed to remove any trace of iron or other contaminants simultaneously separated by the plasma treatment of the powder.

The plasma upgrading of metal powder according to the present invention is an extremely effective method for the removal of halide salt contaminants, especially of NaCl, which typically is about 0.15 weight per cent for commercial grade titanium and about 0.5 weight per cent for zirconium. However, other concentrations significantly above these typical values as well as concentrations measured in terms of a few hundred ppm or less are viewed as being equivalent for purposes of this invention. This process is also considered useful in reducing other undesirable trace contaminants characteristic of titanium, zirconium and hafnium production, including but not limited to Mg, MgCl₂, Na, Fe and Cr containing compounds as well as entrained H₂ (if desired). Preferably to achieve direct separation of the contaminant from the metal the powder temperature produced in the plasma reactor should be above the boiling point of the contaminant but below the boiling point or possibly even the melting point of the base metal powder. Thus for example, the minimum temperature for the separation of NaCl from titanium would be about 1413°C and the maximum would be about 3327°C.

The actual injection of the metal powder into the plasma reactor and into the hot gases issuing from the arc heater (or the like) can be performed by any of the conventional methods known in the art. Preferably a high velocity is required to ensure adequate penetration of the plasma stream. Thus a pressurized inert carrier gas such as argon, helium or the like, as used in establishing the desired plasma jet plume or plasma stream, can also be advantageously used to sweep or inject the metal particles into the plasma. Optional selected reactive gases can be blended with the inert gas stream to achieve a desired chemical

reaction. Thus, the addition of hydrogen to the argon stream to produce titanium hydride or the like during the upgrading process should be considered equivalent for purposes of this invention.

In the broadest sense, the method of the present invention can be employed with any of the known plasma arc heaters independent of the particular type of heating. Thus, the arc heater can be an alternating current or direct current system. Similarly, various alternative apparatuses, as known in the art, can be substituted for the illustrated arc heater.

The advantages associated with the use of the process according to the present invention not only include the purification of the metal powder and the ability to preserve the particle size distribution while controlling the degree of spheroidization, but also the present method is viewed as economically attractive and highly favorable. Routine plasma spheroidization processes typically consume only a few kilowatt hours per pound of injected material. The theoretical minimum amount of energy to melt titanium, for example, is approximately 0.8 kW hr/lb. Thus, including the plasma gas and estimated inefficiencies, the upgrading or extra cost of processing titanium powder according to the present invention is estimated at less than 10 per cent of the current piece of sponge fines. The small additional processing cost is more than justified by the improved quality and the wider applicability of the titanium powder.

95 Claims

1. A process for upgrading metal powder which comprises establishing a plasma within a plasma reactor; feeding powdered titanium, zirconium or hafnium containing at least one alkali metal or alkaline earth metal halide salt contaminant, through said plasma thus effecting a physical separation of said metal and contaminant salt; cooling said metal; and recovering an upgraded metal.

2. A process according to claim 1, wherein the contaminant salt is sodium chloride.

3. A process according to claim 1 or 2, wherein the upgraded metal is quenched within the plasma reactor and thus recovered as an upgraded metal powder.

4. A process according to claim 1, 2 or 3, wherein the physical separation is at a temperature above the boiling point of the contaminant salt, thus at least partially vaporizing said contaminant salt.

5. A process according to claim 4, wherein the physical separation results in said contaminant, at least in part, being present on the surface of the upgraded metal and the surface contaminant is subsequently removed by water washing said upgraded metal.

6. A process for upgrading metal powder as
claimed in claim 1 and substantially as described

herein with particular reference to the
accompanying drawing.

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